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**(54) (Name of the Invention) A MASTER PLATE FOR FLAT PLATE PRINTING AND A  
PRINTMAKING METHOD OF FLAT PLATE PRINTING**

**(57) (Abstract)***(Issue)*

To provide a master plate for flat plate printing and a printmaking method for flat plate printing that allows the creation of a printing plate without processing, while having print durability of the imaging portion, and having no stains in the non-imaging portion, while overlapping of the pressure covering can be limited, and fingerprints and stains in the blanket are not easily generated.

*(Solution)*

A master plate for flat plate printing and a printmaking method for flat plate printing characterized by having a layer that is comprised of photopolymerizing lipophilic thermoplastic monomers/prepolymers and a photopolymerization starter, and a layer that is comprised of a hydrophilic binder in this order on a substrate, and at the same time, having a photothermal conversion agent.

*(Scope of patent claims)*

**(Claim 1)**

A master plate for flat plate printing characterized by having a layer that is comprised of photopolymerizing lipophilic thermoplastic monomers/prepolymers and a photopolymerization starter, and a layer that is comprised of a hydrophilic binder in this order on a substrate, and at the same time, having a photothermal conversion agent.

**(Claim 2)**

A master plate for flat plate printing comprised of a hydrophilic self-film forming filler, photopolymerizing lipophilic thermoplastic monomers/prepolymers, a photopolymerization starter and a photothermal conversion agent.

**(Claim 3)**

A printmaking method for a flat plate characterized by having an image on a printing plate for the flat plate of Claims 1 and 2 be exposed with a high illumination light having a wavelength that said photothermal conversion agent absorbs, and then having a total exposure with active light be carried out to increase the molecular weight of said photopolymerizing lipophilic thermoplastic monomers/prepolymers.

*(Detailed description of the invention)*

**(0001)**

*(Field of the invention)*

The present invention relates to a master plate for flat plate printing and a printmaking method for a flat plate using the master plate for flat plate printing.

**(0002)**

*(Prior art)*

In the past, printmaking systems were extremely troublesome because, for example, a negative or positive film was created from a block copy and next printed on a PS plate on which a photosensitive polymer was coated and then development was carried out to complete the printmaking. Recently, the digitalization of printmaking has rapidly advanced and the means to directly connect an electrical signal from a computer to printmaking has been proposed.

**(0003)**

More specifically, a printmaking method in which an electrical signal from a computer is converted to a laser beam and printed on a photosensitive polymer, and then development is carried out is common; however, it still requires a development process. In addition, inkjet recording and an electronic photo method have been proposed as a method to attach the image-forming material directly on a plate. However, it has a flaw in terms of stable reproducibility and the resolution of the imaging portion.

**(0004)**

As a means of printmaking that achieves stable reproducibility and high resolution and that does not require a development operation, a variety of direct printmaking plates that use a thermal head and laser beam have been proposed. For example, Japanese Unexamined Patent Application Publication S49-118501 discloses a method where the surface of a material that is comprised of a lipophilic resin is chemically treated to form a lipophilic layer, and the lipophilic layer is selectively removed by the laser beam to form

an imaging portion. However, this method consumes a significant amount of energy, has a slow printmaking speed, and in addition, has a low resolution due to the generation of polymer debris and cinder.

(0005)

Japanese Unexamined Patent Application Publication S51-63704 discloses a technology in which a plate material coated with a lipophilic polymer layer that is comprised of non-photosensitive compounds is irradiated with a laser beam to cure the irradiated portion to become hydrophobic or lipophilic, so that it absorbs ink. This method has problems such that it is difficult to strongly and uniformly change the imaging portion, and also, printing stains are easily generated because the water soluble polymer that comprises the non-imaging portion is dissolved during printing.

(0006)

Japanese Unexamined Patent Application Publication H3-108588 proposes a method in which a thermofusing substance that is microcapsulized with pigment is coated on a support, and then the heated portion becomes lipophilic to induce ink absorption. However, there are problems such that the particle diameter of the microcapsules are large, the basic resolution of the obtained prints are low and staining during printing is easily generated because the lipophilic thermofusing material is easily attached to the support and the wall on the plate through the breakdown of the microcapsules.

(0007)

Japanese Examined Patent Application Publication H6-71787 discloses a method in which a sulfonic acid group is introduced on the surface of a plate material that is comprised of a lipophilic polymer to create a non-imaging portion, and the sulfonic acid group on the surface is selectively removed by an irradiating laser beam having a specific energy density to create an imaging portion. However, there is a problem in that staining during the printing is easily generated because the lipophilic polymer layer on the lower surface that is treated with sulfonic acid is partially exposed.

(0008)

Japanese Unexamined Patent Application Publications H7-1849 and H7-1850 propose a thermosensitive flat printing plate that is comprised of a microcapsulized lipophilic compound that is converted to an imaging portion by heat, a hydrophilic layer having a hydrophilic binder polymer, and a support, and the hydrophilic binder polymers are cross-linked in three dimensions so that they are chemically bonded with the lipophilic compound in the microcapsules after the breakdown of the capsules. However, the particle diameter of the obtained microcapsules is large, the general resolution of the obtained print is low, and in principle, the adhesion of the hydrophilic binder polymer and the support is not sufficient. Also the boundary between the lipophilic compound and the hydrophilic binder polymer is not clear, and consequently there still is a problem with staining during printing and a reduction of the resolution.

(0009)

To resolve such problems, Japanese Unexamined Patent Application Publication H9-127683 discloses a flat printing plate wherein a resin particle layer can be made lipophilic by heat on the surface of a hydrophilic substrate. This is in order to employ a technology to convert the hydrophilic portion into a lipophilic portion by heating in an image.

However, there are problems such that when the hydrophilic property prior to the image forming is high, the lipophilic property of the obtained lipophilic image is not sufficient, and conversely when the hydrophilic property prior to the image forming is restrained, a stain is easily generated during printing. In addition, it has a complicated operation, such that for actual use, a peelable anti-drying film is formed on the resin particle layer in order to improve the storage stability of the plate and it requires a peeling process upon printing.

(0010)

The present inventors found a layer that is comprised of a hydrophilic binder, which is formed on a layer that is comprised of a lipophilic thermoplastic resin, and which has changes in the hydrophilic/lipophilic property generated only with exposure to high illumination light, and which is applicable as a printing plate (Japanese Patent Application H10-112262). However, the printing plate obtained through the invention in question had low physical strength and the hydrophilic property of the non-imaging portion easily deteriorated, and consequently it was not appropriate for long-run printing purposes. In addition, fingerprints and stains on the blanket were easily generated and consequently, it did not have satisfactory properties.

(0011)

*(Problem to be solved by the invention)*

The objective of the present invention is to provide a master plate for flat plate printing and a printmaking method for flat plate printing that allows the creation of a printing plate without processing, while having print durability of the imaging portion, and having no stains in the non-imaging portion, while overlapping of the pressure covering can be limited, and fingerprints and stains in the blanket are not easily generated.

(0012)

*(Means for solving the problem)*

The above-mentioned objective of the present invention has been achieved with the following structure.

(0013)

(1) A master plate for flat plate printing characterized by having a layer that is comprised of photopolymerizing lipophilic thermoplastic monomers/prepolymers and a photopolymerization starter, and a layer that is comprised of a hydrophilic binder in this order on a substrate, and at the same time, having a photothermal conversion agent.

(0014)

(2) A master plate for flat plate printing comprised of a hydrophilic self-film forming filler, photopolymerizing lipophilic thermoplastic monomers/prepolymers, a photopolymerization starter and a photothermal conversion agent.

(0015)

(3) A printmaking method for flat plate printing characterized by having an image on a printing plate for the flat plate of said 1 and 2 be exposed with a high illumination light having a wavelength that said photothermal conversion agent absorbs, and then having total exposure with active light be carried out to increase the molecular weight of said photopolymerizing lipophilic thermoplastic monomers/prepolymers.

(0016)

The present invention is described in detail as follows. First, the photopolymerizing lipophilic thermoplastic monomer/prepolymer is described. The present invention has the characteristics of being comprised of a photopolymerizing monomer/prepolymer as a lipophilic thermoplastic substance, which provides a printing plate where it is hard to generate printing stains and that has high printing durability. As such a photopolymerizing monomer/prepolymer, a publicly known lipophilic monomer/prepolymer having ethylene unsaturated bonding that is polymerizable with an active light can be used without limitation.

(0017)

Examples of specific monomer/prepolymers are, mono-functional acrylic esters and their derivatives such as 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate; or compounds in which these acrylates are substituted with methacrylate, itaconate, crotonate, maleate, etc.; bifunctional acrylic esters and their derivatives such as polyethylene glycol diacrylate, pentaerythritol diacrylate, bisphenol A diacrylate, the diacrylate of the  $\epsilon$ -caprolactone adduct of hydroxyphenyl neopentyl glycol; or compounds in which these acrylates are substituted with methacrylate, itaconate, crotonate, maleate, etc.; multi-functional acrylic esters and their derivatives such as trimethylolpropanetriol (met)acrylate, dipentaerythritolhexa acrylate, pyrogallol triacrylate, etc.; or compounds in which these acrylates are substituted with methacrylate, itaconate, crotonate, maleate, etc. In addition, resins having ethylene unsaturated bonding, namely a so-called prepolymer may be appropriately used by introducing acrylic acid or metacrylic acid to an appropriate molecular weight of an oligomer to add photopolymerization. Other than the above, the compounds disclosed in Japanese Unexamined Patent Application Publication S61-6649 and S62-173295 can be used. Furthermore, the compounds disclosed on pages 286 to 294 of "Chemical Products of 11290", The Chemical Daily Co., Ltd., and the compounds disclosed on pages 11 to 65 of the "UV/EB Curing Handbook (Material)", Kobunshi Kankokai, can be appropriately used in the present invention. Among these, monomers/prepolymers that are solid at room temperature can be preferably used.

(0018)

In addition to the compounds having the above-mentioned ethylene unsaturated bonding, the photopolymerizing lipophilic thermoplastic monomer/prepolymer of the present invention is comprised of the following polymerization starter.

(0019)

The polymerization starter of the present invention is to cure the photopolymerizing monomer/prepolymer through exposure, and publicly known photopolymerization starters, and thermopolymerization starters in the case of a photothermal conversion photosensitive layer, can be used. As a photopolymerization starter, the compounds disclosed on pages 39 to 48 of the "Photopolymer Handbook" (Photopolymer Konwakai, Kyogyo Chosakai Publishing Co., Ltd., 1989) can be preferably used individually or in combination of two or more kinds. Examples of thermopolymerization starters are organic peroxides, such as cumene hydroperoxide, tertiary butyl hydroperoxide, dicumyl peroxide, di-tertiary-butyl peroxide, benzoyl peroxide, acetyl peroxide, lauroyl peroxide; azo compounds such as azobisisobutyronitriles; ludox copolymerization starters such as

bivalence iron salt of hydrogen peroxide, persulfate and sodium hydrogen sulfate, cumene hydroperoxide and bivalence iron salt, benzoyl peroxide and dimethylaniline, and in addition, organic metal complexes such as disulfide compounds, manganese triacetylacetonate, pentacyanobenzyl cobaltate can be used. The mixture rate of these polymerization starters is not specifically limited; however, preferably, it is 1 to 20 weight/parts (more desirably 10 weight/parts or less) per 100 weight/parts of a compound that allows addition polymerization or cross-linking.

(0020)

Optionally, the photopolymerizing lipophilic thermoplastic monomer/prepolymer of the present invention can be comprised of other compositions such as a sensitizer, photothermal conversion agents or a polymerization promoter to the extent that they do not hinder the objectives.

(0021)

Examples of sensitizers are triazine compounds such as disclosed in Japanese Unexamined Patent Application Publication S64-13140, aromatic onium salt such as disclosed in Japanese Unexamined Patent Application Publication S64-13141, aromatic halonium salt, organic peroxide such as stipulated in Japanese Unexamined Patent Application Publication S64-13143, bisimidazole compounds such as disclosed in Japanese Unexamined Patent Application Publication S45-37377 and United States Patent 3,652,275, and thiols. 10 weight/parts or less, and preferably 0.01 to 5 weight/parts of sensitizer per a total of 100 weight/parts of photopolymerizing lipophilic thermoplastic monomer/prepolymer is added.

(0022)

As a polymerization promoter, a polymerization promoter or a chain transfer catalyst represented by an amine compound or sulfur compounds (thiol, disulfide, etc.) can be added.

(0023)

Specific examples of polymerization promoters and chain transfer catalysts that can be added to the photopolymerizing compound of the present invention are amines such as N-phenyl glycine, triethanolamine, N, N-diethylaniline; thiols such as stipulated in United States Patent 4,414,312 and Japanese Examined Patent Application Publication S64-13144; disulfides such as disclosed in Japanese Unexamined Patent Application Publication H2-29161; thiones such as disclosed in United States Patent 3,558,322 and Japanese Unexamined Patent Application Publication S64-17048; O-acylthiohydroxamate and N-alkoxypyridinethione such as disclosed in Japanese Unexamined Patent Application Publication H2-291560. An example of a specifically preferable amine compound is N, N-diethylaniline and an example of a sulfur compound is 2-mercaptobenzothiazole.

(0024)

A publicly known photothermal converting agent can be used for the present invention. In a preferable embodiment of the present invention, it is heated by irradiation from a semiconductor laser beam, and therefore a near-infrared light absorbent that demonstrates maximum absorption in the wavelength range of 700 to 3,000 nm is preferred. Carbon

black, etc., is also desirable because it has absorption from the visible to near-infrared range.

(0025)

Organic compounds, for example, coloring matters such as cyanines, polymethines, azuleniums, squaliums, thiopyryliums, naphthoquinones, anthraquinones, etc., and organic metal metallic complexes such as phthalocyanines, azos, thioamides can be appropriately used as a near-infrared absorbent and more specifically, they are compounds disclosed in Japanese Unexamined Patent Application Publications S63-139191 and S64-33547, Japanese Unexamined Patent Application Publications H1-160683, H1-280750, H1-293342, H2-2074, H3-26593, H3-30991, H3-34891, H3-36093, H3-36094, H3-36095, H3-42281, H3-97589 and H3-103476, etc. These can be used individually or by combining two or more kinds.

(0026)

A photothermal converting agent can be present either in the same layer as the photopolymerizing lipophilic thermoplastic monomers/prepolymers, or an adjacent layer, but preferably it should be present in the same layer as the photopolymerizing lipophilic thermoplastic monomers/prepolymers, and it is further desirable that it is present in a form that is compatible with the photopolymerizing lipophilic thermoplastic monomers/prepolymers.

(0027)

As a thermal polymerization inhibitor, compounds such as quinines and phenols can be desirably used. Examples are hydroquinone, pyrogallol, p-methoxyphenol, catechol,  $\beta$ -naphthol, 2, 6-di-t-butyl-p-cresol, etc. 10 weight/parts or less and more preferably 0.01 to 5 weight/parts per 100 weight/parts of photopolymerizing lipophilic thermoplastic monomers/prepolymers is added.

(0028)

When the photopolymerizing lipophilic thermoplastic monomers/prepolymers are used in the form of particles, as an example, particle dispersion is prepared with the following process.

(0029)

A photopolymerization starter, a photothermal conversion agent, thermal polymerization inhibitors, etc., are mixed with the photopolymerizing lipophilic thermoplastic monomers/prepolymers as required. During the mixing, it can be heated as required in order to promote compatibility. While the obtained photopolymerizing lipophilic thermoplastic monomers/prepolymers as above are being stirred at a high speed, they are added to a non-compatible liquid (such as water), and consequently, particle dispersion can be obtained. It is preferable that a surfactant is mixed in the liquid in advance. In addition, it may be added while being chilled.

(0030)

Examples of hydrophilic binders used in the present invention are polyvinyl alcohol, polysaccharide, polyvinylpyrrolidone, polyethylene glycol, gelatin, glia, casein, hydroxyethyl cellulose, carboxymethyl cellulose, methyl cellulose, hydroxyethyl starch, saccharose octaacetate, ammonium alginate, sodium alginate, polyvinyl amine,

polyallylamine, polystyrene sulfonate, polyacrylate, aqueous polyamide, maleic anhydride copolymers, etc.

(0031)

Among the above, the preferable hydrophilic binders are gelatin, polyvinyl alcohol, and carboxymethyl cellulose and the most preferably used hydrophilic binders are gelatin and polyvinyl alcohol.

(0032)

Gelatin, polyvinyl alcohol and carboxymethyl cellulose that are preferably used in the present invention are described as follows.

(0033)

Examples of polyvinyl alcohols are, in addition to polyvinyl alcohols with various degree of polymerization, copolymerized polyvinyl alcohols, random co-polymer of anion modified polyvinyl alcohols that are modified with anions such as carboxyl group and sulfo group, cation modified polyvinyl alcohols that are modified with cations such as ammonium group, silanol modified polyvinyl alcohols, alkoxyl modified polyvinyl alcohols, epoxy modified polyvinyl alcohols, thiol modified polyvinyl alcohols, etc. that are comprised of 50 mol% or greater polyvinyl alcohol skeleton; polyvinyl alcohols in which only the terminal group is anion modified, cation modified, thiol modified, silanol modified, alkoxyl modified and epoxy modified, block-copolymerized polyvinyl alcohol in which aqueous monomers such as acrylic amid and acrylate are introduced, graft-copolymerized polyvinyl alcohol in which silanol group, etc., are grafted, and co-polymerized polyvinyl alcohol in which reactive group such as  $(-\text{COCH}_2\text{COCH}_3)$  is introduced.

(0034)

The preferable polyvinyl alcohol is one having a saponification of 70 mol% or greater. More preferably it is 85 mol% or greater and most preferably 90% or greater. Polyvinyl alcohol with high saponification is preferable because it allows modification of crystalline by thermal process and consequently, water resistance property is added.

(0035)

As a co-polymerized polyvinyl alcohol, the following monomers can be used as a co-polymerized monomer.

(0036)

(1) Monomers having an aromatic hydroxyl group: for example, o-hydroxy styrene, p-hydroxy styrene, m-hydroxy styrene, o-hydroxyphenyl acrylate, p-hydroxyphenyl acrylate, m-hydroxyphenyl acrylate, etc.

(0037)

(2) Monomers having an aliphatic hydroxyl group: for example, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, N-methyrol acrylic amid, N-methyrol metacrylic amid, 4-hydroxybutyl methacrylate, 5-hydroxypentyl acrylate, 5-hydroxypentyl methacrylate, 6-hydroxyhexyl acrylate, N-(2-hydroxyethyl) acrylic amid, N-(2-hydroxyethyl) metacrylic amid, hydroxyethylvinylether, etc.

(0038)

(3) Monomers having an aminosulfonyl group: for example, m-aminosulfonylphenyl methacrylate, p-aminosulfonylphenyl methacrylate, m-aminosulphonylphenyl acrylate, p-aminophenyl acrylate, N-(p-aminosulphonylphenyl) methacrylic amid, N-(p-aminosulphonylphenyl) acrylic amid, etc.

(0039)

(4) Monomers having a sulfonamide group: for example, N-(p-toluenesulfonyl) acrylic amid, N-(p-toluenesulfonyl) methacrylic amid, etc.

(5)  $\alpha,\beta$ -unsaturated carboxylic acids: for example, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, itaconic anhydride, etc.

(0040)

(6) Substituted or non-substituted alkyl acrylates: for example, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, heptyl acrylate, octyl acrylate, nonyl acrylate, decyl acrylate, undecyl acrylate, dodecyl acrylate, benzyl acrylate, cyclohexyl acrylate, acrylate-2-chloroethyl, N, N-dimethylaminoethyl acrylate, glycidyl acrylate, etc.

(0041)

(7) Substituted or non-substituted alkyl methacrylates: for example, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, heptyl methacrylate, octyl methacrylate, nonyl methacrylate, decyl methacrylate, undecyl methacrylate, dodecyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, methacrylate-2-chloroethyl, N, N-dimethylaminoethyl methacrylate, glycidyl methacrylate, etc.

(0042)

(8) Acrylic amids or methacrylic amids: for example, acrylic amid, methacrylic amid, N-ethylacrylic amid, N-hexylacrylic amid, N-cyclohexylacrylic amid, N-phenylacrylic amid, N-nitrophenylacrylic amid, N-ethyl-N-phenylacrylic amid, N-(4-hydroxyphenyl) acrylic amid, N-(4-hydroxyphenyl) acrylic amid, N-(4-hydroxyphenyl) methacrylic amid, etc.

(0043)

(9) Monomers having a fluorine alkyl group: for example, trifluoroethyl acrylate, trifluoroethyl methacrylate, tetrafluoropropyl methacrylate, hexafluoropropyl methacrylate, octafluoropentyl acrylate, octafluoropentyl methacrylate, heptadecafluorodecyl methacrylate, N-butyl-N-(2-acryloxyethyl) heptadecafluorooctylsulfon amid, etc.

(0044)

(10) Vinyl ethers: for example, ethylvinyl ether, 2-chloroethylvinyl ether, propylvinyl ether, butylvinyl ether, octylvinyl ether, phenylvinyl ether, etc.

(0045)

(11) Vinyl esters: for example, vinyl acetate, vinyl chloroacetate, vinyl butylate, vinyl benzoate, etc.

(0046)

(12) Styrenes: for example, styrene, methyl styrene, chloromethyl styrene, etc.

(0047)

(13) Vinyl ketones: for example, methylvinyl ketone, ethylvinyl ketone, propylvinyl ketone, phenylvinyl ketone, etc.

(0048)

(14) Olefins: for example, ethylene, propylene, isobutylene, butadiene, isoprene, etc.

(0049)

(15) N-vinyl pyrrolidone, N-vinyl carbazole, 4-vinyl pyridine, etc.

(0050)

(16) Monomers having a cyano group: for example, acrylonitrile, methacrylonitrile, 2-pentenitrile, 2-methyl-3-butenitrile, 2-cyanoethyl acrylate, o-cyanostyrene, m-cyanostyrene, p-cyanostyrene, etc.

(0051)

(17) Monomers having an amino group: for example; N, N-diethylaminoethyl methacrylate; N, N-dimethylaminoethyl acrylate; N, N-dimethylaminoethyl methacrylate; polybutadiene urethane acrylate; N, N-dimethylaminopropyl acrylic amid; N, N-dimethyl acrylic amid; actyloymorpholine; N-isopropyl acrylic amid; N, N-diethyl acrylic amid; etc.

(0052)

The preferable polyvinyl alcohols are reactive group introduced polyvinyl alcohol and anion group introduced polyvinyl alcohol. In particular, reactive group introduced polyvinyl alcohol is desirable. Examples of reactive group are, silanol group, acetoacetyl group, thiol group and epoxy group. Among these reactive groups, silanol group, acetoacetyl group and thiol group are specifically desirable.

(0053)

The above-mentioned polyvinyl alcohol can be used individually or in combination of two or more kinds.

(0054)

In addition, when polyvinyl alcohol is used, other polymer or one or two or more types of mold lubricant can be used with a main ingredient of the above-mentioned polyvinyl alcohol. Furthermore, two or more polymers and mold lubricants can be used together.

(0055)

Specific examples of polymers are natural polymers such as starch, processed starch, casein, glia, gelatin, Arabian gum, sodium alginate, pectin; semi-synthesized polymers such as carboxymethyl cellulose, methyl cellulose, viscose, etc.; synthesized polymers such as polyacrylamid, polyethylene imine, sodium poly acrylate, polyethylene oxide, polyvinylpyrrolidone; and compounds disclosed in Japanese Unexamined Patent Application Publication H4-176688. As a specific mold lubricant, for example, a compound disclosed in Japanese Unexamined Patent Application Publication H4-186354 can be appropriately used.

(0056)

In addition, in order to improve the property of polyvinyl alcohol, compounds such as antistatic agent or surfactant, etc., can be added. More specifically, for example, compounds stipulated in Japanese Unexamined Patent Application Publication H4-184442 can be appropriately used. These can be used individually or in combination of two or more kinds.

(0057)

When polyvinyl alcohol is used, the preferred film thickness of the thermosensitive layer is 30  $\mu\text{m}$  or less and more desirably, 0.01 to 3  $\mu\text{m}$ .

(0058)

Examples of gelatin are alkaline treated gelatin, acid treated gelatin, modified gelatin (for example modified gelatins disclosed in Japanese Examined Patent Application Publication S38-4854, S40-12237, specification of UK Patent 2,525,753, etc.) and these can be used individually or in combination of two or more kinds. For example, in addition to lime treated gelatin, acid treated gelatin can be used and also hydrolyzed gelatin and enzyme treated gelatin disclosed in Bull. Soc. Sci. Photo. Japan. No. 16. P 30 (1966) can be used.

(0059)

Examples of carboxymethyl cellulose are carboxymethyl cellulose and its salts, such as sodium salt, calcium salt, potassium salt, aluminum salt, magnesium salt, ammonium salt. Among these carboxymethyl cellulose, sodium carboxymethyl cellulose, and ammonium carboxymethyl cellulose are preferable. In particular, ammonium carboxymethyl cellulose is desirable. It is desirable because when these are used, although it is water soluble, solubility to water is reduced when it is coated on the support and dried.

(0060)

It is preferable that a hydrophilic bonding agent is used in the range of 10 to 98 weight% in a layer comprising said bonding agent. The more desirable amount of the hydrophilic bonding agent is 20 to 97 weight% and even more preferably, it is 30 to 96 weight%.

(0061)

Next, the hydrophilic self-film forming fillers used in the present invention are described as follows. There are hydrophilic self-film forming fillers that are a salt of a synthetic resin and that are a basic substance having an acid value, which have a hydrophilic group such as a hydroxyl group as a substituent. In order to have fine particles of water dispersible resin particles, and to add a large hydrophilic property to the particles while preventing dissolution and the swelling of the particles, it is preferable to use a synthetic resin with an acid value of 50 or greater and 280 or less and have at least a portion of it be neutralized with a base. In particular, in order to prevent the fusion of said resin particles, it is preferable for the glass transition temperature of the resin to be 50  $^{\circ}\text{C}$  or greater and it is further preferably for it to be 70  $^{\circ}\text{C}$  or greater.

(0062)

More specifically, there is a copolymer that is comprised of at least one or more monomer units selected from, for example, substituted styrenes such as styrene or  $\alpha$ -methyl styrene; acrylates such as methylester acrylate ethylester acrylate, butylester acrylate, 2-ethylhexylester acrylate; methacrylates such as methylester methacrylate, ethylester methacrylate, butylester methacrylate, 2-ethylhexylester methacrylate. In

addition, although there is no limit to the range of the molecular weight of the resin, ones with a molecular weight of 1,000 or greater and 100,000 or less are more preferable.

(0063)

In addition, as a means to improve cohesion, abrasion resistance, oilproofing and the alkaline proofing property of the imaging portion and the prevention of the fusion of particles of the non-imaging portion, it is preferable that the hydrophilic self-film forming filler is an ionomer resin having a structure such that at least a portion of the total amount of the functional group, which gives an acid value to the synthetic resin, crosslinks between molecules via the polyvalence metal ion and is unified.

(0064)

Any valence number for the polyvalence metal ion used for the ionomer resin can be chosen as long as it is 2 or greater; however, preferably it is 2 or 3, and more preferably, the resin particles obtained by selecting one or more of calcium ions, barium ions, magnesium ions, zinc ions or aluminum ions have no color, have a lower toxicity and demonstrate a strong and superior thermal plasticity. Cross-linking of the resin by these polyvalent metal ions is carried out preferably with a polyvalent metal ion having an amount that is a 10% to 30% equivalent of the anion functional group, and consequently, the ionomer resin water dispersion has less gelation of the synthetic resin and is stable. Also, it has a low reduction of the thermal hydraulics property of the resin particles.

(0065)

In addition, as a hydrophilic self-film forming filler, self-film forming inorganic ultra-fine particles can be used. Examples of the inorganic ultra-fine particles of the present invention are silica (colloidal silica), water glass, alumina or hydrated alumina (alumina sol, colloidal alumina, aluminum polyhydroxide, cationy aluminum oxides and hydrates thereof, pseudo boemite, etc.), surface treated cationy colloidal silica, zircon, zircon hydroxide, zircon fluoride, aluminum silicate, magnesium silicate, calcium carbonate, barium carbonate, barium sulphate, titanium dioxide, zirconium oxide, iron oxide, zinc oxide, tin oxide, magnesium oxide, antimony oxide, niobium oxide, cerium oxide, etc. These inorganic ultra-fine particles are, in general, used by being dispersed in a solvent in a colloid state while the primary particle diameter is being maintained. Specific examples of colloidal silica are Catalloid S series (Catalysis Research Center), Fine Catalloid F-120, USBB-120, etc., (Catalysis Research Center), Ludox series (Du Pont), Snowtex series (Nissan Chemical Co., Ltd.). Specific examples of alumina sol are Catalloid A series (Catalysis Research Center), Alumina sol (Nissan Chemical Co., Ltd.), Nanowhisker series (Daiichi Kigenso Kagaku Kogyo Co., Ltd.), etc.

(0066)

Inorganic ultra-fine particles can be used individually or in combination of two or more kinds. A preferable combination is a combination of fine particles having the same types of skeleton. For example, it is preferable to use ultra-fine particles of colloidal silica with an average particle diameter of 3 to 25 nm and ultra-fine particles of colloidal silica with an average particle diameter of 50 to 100 nm in combination, etc. As described above, upon usage, it is preferable to use particles with a smaller particle diameter, and the preferable amount to be added is 50 to 100%, and more preferably, 60 to 100%, and even more preferably 70 to 100%. In addition, it can be used together with a hydrophilic binder.

(0067)

Examples of inorganic fine particles are fine particles of zinc oxide, titanium oxide, barium sulphate and silica (silicon oxide). A method in which fine particles are obtained by crushing and dispersing in solvent using a dispersion method such as a sand mill or a ball mill can be employed as a manufacturing method for inorganic fine particles. When fine particles are obtained by crushing and dispersing in a solvent using a dispersion method such as a sand mill or ball mill, it is desirable to use an appropriate dispersing agent regardless of whether they are organic fine particles or inorganic fine particles.

(0068)

As long as it is within a range that does not inhibit the purpose of the present invention, publicly known inorganic fine particles can be used. Examples of such inorganic fine particles are precipitated calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulphate, barium sulphate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatom earth, calcium silicate, synthesized amorphous silica, aluminum hydroxide, lithopone, zeolite, hydrolyzed halloysite, magnesium hydroxide, synthesized mica, etc. Among these inorganic fine particles, inorganic porous fine particles are preferable and examples of such inorganic porous fine particles are porous synthesized amorphous silica, porous calcium carbonate, porous alumina, etc. In particular, synthesized porous amorphous silica with a large pore volume is preferable.

(0069)

For the plate for the flat plate printing of the present invention, the strength of the imaging portion was improved by using photopolymerizing lipophilic thermoplastic monomers/prepolymers and by polymerizing the photopolymerizing lipophilic thermoplastic monomers/prepolymers after the image is exposed.

(0070)

The hydrophilic layer of the present invention is provided on said imaging portion and plays the role of having a hydrophilic property, namely it improves the anti-stain function during printing. It is perforated and removed in the shape of the image by ablation due to laser exposure, and at the same time, the surface of the recording surface, which was changed from hydrophilic to hydrophobic is exposed, widening the difference between the hydrophilic and lipophilic properties.

(0071)

It is preferable that the hydrophilic layer is a thin film allowing easy ablation or allowing permeation of a lipophilic substance; however, when it is too thin, the effect for the hydrophilic layer cannot be obtained. The preferable film thickness is 0.1  $\mu\text{m}$  to 2.0  $\mu\text{m}$ . More preferably it is 0.2  $\mu\text{m}$  to 1.0  $\mu\text{m}$ . When the film thickness is greater than 2.0  $\mu\text{m}$ , removal of the hydrophilic layer with laser ablation or penetration of the lipophilic substance may not be sufficient. When the film thickness is less than 0.1  $\mu\text{m}$ , strength of the hydrophilic layer becomes insufficient; consequently, stains may be generated during the printing.

(0072)

It is preferable for the hydrophilic layer to be 20 or greater for the hydrogen bonding component (H) of the surface energy  $\gamma$  and 40 or less for the cohesive power (d) of said surface energy  $\gamma$ .

(0073)

It is preferable to roughen the recording layer side or the opposite side of the plate material for the flat plate printing of the present invention. Although the method of roughing is arbitrary, when roughening is carried out by coating, as long as it does not have a substantial adverse effect physically or chemically on the material for the flat plate printing, any coating solution is acceptable. For example, the roughened layer can be a mechanically matted layer or a resin layer that is comprised of a matting agent. As mechanical matting methods, there are 1) having the roughening layer be coated so that a coated layer with a rough pattern can be obtained and 2) mechanical roughening to create a roughened layer.

(0074)

Specific examples of 1) are a method in which a roughened layer is coated with a gravure roll having a rough pattern or a method in which a rough pattern is obtained by spraying resin particles and thermally fusing.

(0075)

A specific example of 2) is a method wherein after a rough layer is provided, pressure is applied with a pressuring roller having a rough surface with a higher hardness than the hardness of the rough layer to make it a matte. The support itself can be made to be a matte by applying pressure.

(0076)

When a metal support is not used as the support, by containing an electrical conduction agent on the rough layer on the back surface, the usability can be improved.

(0077)

The preferable film thickness of rough layer is 20 to 30  $\mu\text{m}$ . When the rough layer is thinner than 2  $\mu\text{m}$ , or thicker than 30  $\mu\text{m}$ , it is difficult to obtain desired roughness.

(0078)

In the case a resin containing matting agent is used, the desirable particle diameter of the particles of the matting agent is in the range of 1 to 30  $\mu\text{m}$  and in particular it is desirable for it to be 2 to 10  $\mu\text{m}$ .

(0079)

As a filler that is used as a matting agent, solid particles that are similar to the ones used for the recording layer can be used.

(0080)

As a support of the plate for the flat plate printing of the present invention, publicly known supports can be used without particular limitation. Depending on the purpose, the material, layer structure and size are selected for use. Examples are a variety of papers such as paper, coated paper, synthesized paper (polypropylene, polystyrene, materials thereof combined with paper); a variety of plastic film or sheet used individually or in

combination of two or more kinds, which are selected from vinyl chloride resin sheet, ABS resin sheet, polyethylene terephthalate (PET) film, polybutylene terephthalate film, polyethylene naphthalate (PEN) film, polyarylate film, polycarbonate film, polyetherketone film, polysulfone film, polyethersulfone film, polyimide film, polyethylene film, polypropylene film, etc.; film or sheet made of a variety of metals; film or sheet made of a variety of ceramics; metal plates such as aluminum, stainless steel, chromium, nickels, etc.; resin coated paper that is laminated or deposited with a thin film of metal.

(0081)

When it is a support with a hydrophobic surface, a hydrophilic process can be applied to the surface. Preferable examples of hydrophilic process are sulfate treatment, oxygen plasma etching process, corona discharging process, and coating with an aqueous resin.

(0082)

The drying temperature is 30 to 100 °C and preferably 30 to 80 °C, and even more preferably from 30 to 70 °C. The preferable drying time is 30 seconds to 10 minutes and is more preferably in the range of 1 to 5 minutes.

(0083)

On the plate for the flat plate printing of the present invention, a variety of backing layers to prevent curling and to prevent adhering during the layering immediately after the printing can be used.

(0084)

It is desirable for the average roughness at the centerline  $R_a$  to be 0.1 to 0.5  $\mu\text{m}$  on the recording layer surface of the plate for the flat plate printing obtained as above. When it is less than 0.1  $\mu\text{m}$ , there may be problems with water retention, transportation and blocking properties. This  $R_a$  can be, for example, measured using RST/PLUS (manufactured by Wyco).

(0085)

Examples of methods to form an image on the plate for the flat plate printing of the present invention are a method to directly apply thermal energy in the shape of the image using a thermal head, etc., and a method in which energy with a high output light is irradiated in the shape of the image and it is applied by converting it to a thermal energy.

(0086)

The method in which thermal energy is directly applied in the shape of the image using a thermal head, etc., is desirable mainly for inexpensive low resolution line drawing. In contrast, the method in which energy from a high power light is irradiated in the form of an image and applied by converting it to thermal energy is desirable mainly for high resolution or half tone images such as in commercial printing, because it easily allows highly precise writing.

(0087)

When a laser is used for the exposure, the light can be focused in a beam and this allows a scanning exposure that corresponds to the image data. Consequently, it allows direct writing without using a masking material. When a laser is used as the light source, it easily allows focusing in the exposure area on a microscale, allowing the formation of an

image formation with a high resolution. Any one of, for example, argon lasers, He-Ne gas lasers, YAG lasers or semiconductor lasers, can be appropriately used as the light source of the laser.

(0088)

Among those, use of a semiconductor laser or a YAG laser is more preferable to the extent that a high output power that is appropriate for the plate for the flat plate printing of the present invention can be combined in a compact device at a relatively inexpensive price.

(0089)

Examples of the scanning exposure method of a laser are exposure methods such as external barrel scanning, internal barrel scanning and flat plate scanning. During the external barrel scanning, irradiation by a laser is carried out while a drum, where recording material is coiled around the outside, is rotated. In this case, rotation of the drum is for horizontal scanning and the movement of the laser beam is for vertical scanning. During the internal barrel scanning, a laser beam is irradiated from inside while recording material is set inside the drum. In this case, by rotating a partial or entire optical system, horizontal scanning is carried out in the direction of the circumference. Then, by linearly moving a part of or the entire optical system parallel to the axis of the drum, vertical scanning in the direction of the axis is carried out. During flat plate scanning, by combining a polygon mirror and an optogalvanic mirror with an f $\theta$  lens, etc., horizontal scanning is carried out and vertical scanning is carried out by moving the recording medium. External barrel scanning and internal barrel scanning have extremely high precision optical systems and are appropriate for high density recording.

(0090)

Examples of light source for the total exposure are, lasers, light emitting diodes, xenon flash lamps, halogen lamps, carbon arc lamps, metal halide lamps, tungsten lamps, high-pressure mercury lamps, non-electrode light sources, etc.

(0091)

Image formation (printmaking) on a plate for the flat plate printing of the present invention is possible using only the above-mentioned image exposure and is characterized by not requiring a removal process for the non-image portion through developing using a solution, unlike the traditional method. Therefore, image formation on the plate for flat plate printing can be carried out with a designated exposure device, and also the obtained flat printing plate can be used by setting it in a printer. In addition, image formation can be carried out on a plate drum and a directly printable system.

(0092)

#### *Examples of Embodiment*

The present invention is described in detail with embodiments. The present invention is not limited by these embodiments. In the following, "parts" means "weight/parts".

(0093)

#### *Embodiment 1*

Preparation of photopolymerizing thermoplastic lipophilic particles.

The following compositions were heated to 80 °C while being stirred and fused with each other.

Photopolymerizing monomer (NK ester 23G: Shin Nakamura Chemical Co., Ltd.)	15.0 g
Photopolymerization starter (diisopropylthioxanthone)	3.0 g
Sensitizer (dimethyl benzoate isoamyl)	2.0 g
Thermal polymerization inhibitor (hydroquinone)	0.015 g
Infrared absorbing color (CY-10: Nippon Kayaku Co., Ltd.)	5.0 g

The above-mentioned melt was added at a speed of 2 cc/min. to the following water containing activator while being stirred with a homogenizer at a speed of 10,000 rpm and dispersed.

(0094)

Ion-exchange water	40.0 g
Emulgen 935	1.0 g

The average particle diameter of the obtained resin particle was 2.3  $\mu$ .

(0095)

Preparation of a plate for flap plate printing

A coating solution with the following composition is coated on a PET film that is preprocessed with gelatin so that the film thickness becomes 5  $\mu$ m and a photopolymerizing lipophilic layer is formed. The following values indicate weight/parts.

(0096)

Recording layer	
Abovementioned dispersion	50 Solid content
Polyvinyl alcohol (GL-5: Nippon Gohsei)	10 Solid content
Hydrophilic layer	

A hydrophilic layer with the following composition is coated on top of the above so that the film thickness becomes 1  $\mu$ m.

(0097)

Colloidal silica (Snowtex S: Nissan Chemical, Co., Ltd.)	50 Solid content
Polyvinyl alcohol (GL-5: Nippon Gohsei)	20 Solid content
Silica particles ((Thyroid) 435)	30 Solid content

*Embodiment 2*

Instead of the recording layer GL-5 in Embodiment 1,

Colloidal silica (Snowtex S: Nissan Chemical, Co., Ltd.)	50 Solid content
Silica particles ((Thyroid) 435)	30 Solid content

were added and coated so that the film thickness becomes 8  $\mu\text{m}$ .

(0098)

*Embodiment 3*

Instead of the photopolymerizing thermoplastic lipophilic particles of the recording layer in Embodiment 1, the photopolymerizing thermoplastic lipophilic melt was coated without being dispersed so that the film thickness becomes 5  $\mu\text{m}$ , and on top of this,

Colloidal silica (Snowtex S: Nissan Chemical, Co., Ltd.)	50 Solid content
Polyvinyl alcohol (GL-5: Nippon Gohsei)	20 Solid content
Silica particles ((Thyroid) 435)	30 Solid content
Fluorine surfactant: (Dainippon Ink and Chemicals, Inc.: FC-430)	1 Solid content

were coated as a hydrophilic layer so that the film thickness becomes 1.5  $\mu\text{m}$ .

(0099)

*Comparative Example 1*

(0100)

The recording layer in Embodiment is substituted with the following coating solution and coated so that the film thickness becomes 5  $\mu\text{m}$ .

Polyvinyl alcohol (GL-5: Nippon Gohsei)	20 Solid content
Wax emulsion (A-101: Gifu Shellac Co., Ltd.)	50 Solid content

A coating solution in Embodiment 1 is coated as a hydrophilic layer so that the film thickness becomes 1  $\mu\text{m}$ . The recording layer in Embodiment 1 is substituted with the following coating solution and it was coated so that the film thickness becomes 8  $\mu\text{m}$ .

(0101)

*Comparative example 2*

(0102)

Reactive polyvinyl alcohol (Z-100: Nippon Gohsei Co., Ltd.)	20 Solid content
Silica particles ((Thyroid) 435)	30 Solid content
Photopolymerizing thermoplastic lipophilic particles	34 Solid content
Melamine Resin (Sumirez Resin 613: Sumitomo Chemical Co., Ltd.)	2 Solid content

In this case a hydrophilic layer is not provided.

(0103)

*Comparative example 3*

A recording layer similar to Embodiment 3 was coated and a hydrophilic layer was coated as follows so that the film thickness becomes 1.5  $\mu\text{m}$ .

Reactive polyvinyl alcohol (Z-100: Nippon Gohsei Co., Ltd.)	50 Solid content
Silica particles ((Thyroid) 435)	30 Solid content
Melamine Resin (Sumirez Resin 613: Sumitomo Chemical Co., Ltd.)	5 Solid content
Organic amine salt (Sumirez Accelerator ACX-P: Sumitomo Chemical Co., Ltd.)	1 Solid content

(0104)

*Comparative example 4*

Having the recording layer similar to Comparative example 2 and not having a hydrophilic layer.

(0105)

The obtained material for flat plate printing was irradiated with a printing device having a semiconductor laser with an illumination wavelength of 830 nm and an output of 500 mW and thus recording was carried out by irradiating a variety of exposure energies. The strength of the laser radius was  $1/e^2$ , which was 20  $\mu\text{m}$  at the peak. In addition, the resolution was 1,000, 2,000 and 4,000 dpi in both the scanned direction and for vertical scanning.

(0106)

*<Sensitivity>*

Exposure was carried out under the above-mentioned conditions and an exposure energy value ( $\text{mJ}/\text{cm}^2$ ) that is required for uniform development ink (Fuji Film Co., Ltd.: PI-2) acceptance by the solid typesetting portion was found, and an evaluation was carried out with the exposure energy value.

(0107)

*<Resolution>*

Exposure was carried out under the above-mentioned conditions and an exposure energy value ( $\text{mJ}/\text{cm}^2$ ) that is required for uniform development ink (Fuji Film Co., Ltd.: PI-2) acceptance by the solid typesetting portion was found, and then exposure was carried out

with said exposure energy value. It was observed with a magnifier with power of 100, and a range of well reproduce resolution (line/inch) was visually found and evaluated.  
(0108)

*<Printing durability>*

Exposure was carried out under the above-mentioned conditions and an exposure energy value that is required for uniform ink acceptance by the solid typesetting portion was found, and then exposure was carried with said exposure energy value. An image with 175 lines was created. Then, printing was carried out with a printer (Heidel GTO) using ink (High Plus M Red, manufactured by Toyo Ink Manufacturing Co., Ltd.) and moistening water (SEU-3, manufactured by Konica Corporation, 2.5% solution). The printing was continued until there was an ink defect in the solid typesetting portion of the images of the printing materials, or until the ink adhered to the non-line portion. The number of prints was then calculated and the printing durability was evaluated with this number.

(0109)

*<Printing stain>*

During the evaluation of the above-mentioned printing durability, an evaluation was made as to the amount of paper at which stains started to be generated when water was gradually reduced for the regular water-ink balance during the printing.

(0110)

*<Fingerprint stains>*

Fingerprints were applied by pressing a finger on the non-exposed portion of the exposed printing plate for flat plate printing, and then printing was carried out with a printer (Heidel GTO) on coated papers, using ink (High Plus M Red, manufactured by Toyo Ink Manufacturing Co., Ltd.), and moistening water (Etching solution SG-51 by Tokyo Ink Co., Ltd, Concentration: 1.5%). Then fingerprints due to the transference of ink on the fingerprint on the plate through the blanket were evaluated with the following index.

(0111)

Good: No fingerprint

Fair: Fingerprint is partially observed

Bad: Complete fingerprint is observed

*<Staining of the blanket>*

An exposed printing plate for flat plate printing was set on a printer (Heidel GTO) and printing was carried out using a coated paper, moistening water (Etching solution SG-51 by Tokyo Ink Co., Ltd, Concentration: 1.5%) and ink (High Plus M Red, manufactured by Toyo Ink Manufacturing Co., Ltd.). After the printing of 5,000 pieces, ink stains on the blanket (portion that corresponds to the non-imaging portion on the plate) were peeled with plastic tape, and they were placed on a white paper to visibly compare the degree of staining and an evaluation of the acceptability/defectiveness was carried out.

(0112)

Good: Hardly observed

Fair: Partially observed

Bad: Fully generated

(0113)

(Table 1)

	Embodiment 1	Embodiment 2	Embodiment 3	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Total exposure	30 sec at a illumination of 80 W/cm <sup>2</sup>	30 sec at a illumination of 80 W/cm <sup>2</sup>	30 sec at a illumination of 80 W/cm <sup>2</sup>	30 sec at a illumination of 80 W/cm <sup>2</sup>	30 sec at a illumination of 80 W/cm <sup>2</sup>	30 sec at a illumination of 80 W/cm <sup>2</sup>	None
Sensitivity (mJ/cm <sup>2</sup> )	200	150	180	180	150	180	180
Resolution (line/inch)	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Print durability (10,000 pieces)	100,000	100,000	100,000	200,000	500,000	500,000	200,000
Print stain	80	48	63	80	20	25	80
Fingerprint	Good	Good	Good	Fair	Bad	Bad	Fair
Stain on the blanket	Good	Good	Good	Fair	Bad	Bad	Fair

(0114)

Table 1 demonstrates that the sample of the present invention is a plate for flat plate printing and a printmaking method for flat plate printing that allows the creation of a printing plate without processing, while having print durability of the imaging portion, and having no stains in the non-imaging portion, while overlapping of the pressure covering can be limited, and fingerprints and stains in the blanket are not easily generated.

(0115)

*(Effect of the invention)*

The present invention was able to provide a plate for flat plate printing and a printmaking method for flat plate printing that allows the creation of a printing plate without processing, while having print durability of the imaging portion, and having no stains in the non-imaging portion, while overlapping of the pressure covering can be limited, and fingerprints and stains in the blanket are not easily generated.

Continued from the front Page

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		AD01	AD03	BC81	CA00	CC20		
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	2H096	AA07	AA08	BA05	BA16	BA20		
		CA05	CA20	EA02	EA04	EA13		
		FA02	JA03					
	2H113	AA02	AA03	AA04	BA05	FA16		
		FA42						
	2H114	AA04	AA23	AA24	BA01	DA21		
		DA41						